

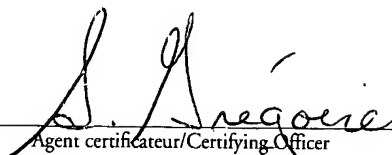
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Specification and Drawings, as originally filed, with Application for Patent Serial No: **2,339,056**, on  
March 2, 2001, by **BAYER INC.**, assignee of William Hopkins, for "Filled Elastomeric  
Compositions".

  
Agent certificateur/Certifying Officer

November 6, 2001

Date

ABSTRACT

Elastomeric compositions comprising natural rubber, halobutyl elastomer, a mineral filler and a bonding agent display improved properties useful, for example, in vehicle  
5 tire treads.

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The present invention relates to elastomeric compositions, to processes for making such compositions and to their use.

#### BACKGROUND OF THE INVENTION

5           Natural rubbers are known to be useful for many purposes, one of which is in vehicle tire treads, especially for truck tires. Many properties are desirable in a rubber for use in a vehicle tire tread and as improvements in one property are achieved this is often at the expense of other properties.

10   For instance, it is desirable that rubber for tire treads shall display good wet traction, good wear characteristics and low rolling resistance. Wet traction correlates with  $\tan \delta$  at 0°. Wear characteristics are measured by the DIN (Deutsche Industrie Norm) abrasion test. Rolling resistance correlates

15   with  $\tan \delta$  or  $E''$  at 60°C. The invention provides compositions in which one or more of these properties can be enhanced without significant deleterious effect on the other.

#### SUMMARY OF THE INVENTION

          According to one aspect, the invention provides an

20   elastomeric composition comprising natural rubber, a halobutyl rubber, a mineral filler, preferably silica, and a rubber-mineral filler bonding agent.

          According to another aspect, the invention provides a process for preparing an elastomeric composition which

25   comprises blending natural rubber and halobutyl rubber with a mineral filler, preferably silica, with a rubber-mineral filler bonding agent, preferably a silane.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

In accordance with the invention, an elastomeric composition is composed of natural rubber and a halobutyl elastomer, and with a mineral filler. Our copending Canadian  
5 Patent Application Serial No. 2,293,149 provides halobutyl elastomer filled with a mineral filler and in a preferred embodiment of this invention the halobutyl elastomer is in accordance with Application Serial No. 2,293,149, the disclosure of which is incorporated by reference.

10 Accordingly, a preferred embodiment of this invention is an elastomeric composition comprising a blend of: (i) natural rubber and (ii) a halobutyl elastomer (iii) a mineral filler, preferably silica, and (iv) a silane that has at least one hydroxyl group or hydrolysable group attached to the  
15 silicon atom of the silane, which elastomeric composition is cured with sulphur.

Natural rubber and halobutyl rubber are both oleophilic. Minerals that find use as filler tend to be oleophobic. It is difficult to achieve good mixing of  
20 oleophobic particles with oleophilic rubber, and a solution to this difficulty is to incorporate an agent, referred to herein as a bonding agent, in the rubber-filler mixture. The bonding agent can be a silane or mixture of silanes. The silane has at least one hydroxyl group or hydrolysable group attached to the  
25 silicon atom of the hydrolysable group attached to the silicon atom of the silane. Particular silanes that can be used include an aminosilane, particularly an aminosilane as described in PCT International Application PCT/CA98/00499, published on 26 November as WO98/53004, or a sulfur-containing  
30 silane as described in United States Patent No. 4,704,414, published European Patent Application No. 0 670 347 A1 or

published German Patent Application No. 4,435,311 A1, the disclosures of which are incorporated by reference. It is of course possible to use a mixture of carbon black filler and a mineral filler. Mineral fillers are discussed in greater  
5 detail below.

The halobutyl elastomer and natural rubber may be in admixture with one or more further elastomers or elastomeric compounds. The halobutyl elastomer should constitute more than 5% of any such mixture. In some cases it is preferred not to  
10 use such further elastomers but to use the halobutyl elastomer and natural rubber as the sole elastomers. If further elastomers are to be used, however, then the further elastomer may be, for example, polybutadiene, styrene-butadiene or polychloroprene or an elastomer compound containing one or more of  
15 these elastomers.

Compositions containing only natural rubber and halobutyl rubber as elastomers, and in which the halobutyl elastomer constitutes from 5 to 50%, particularly 5 to 30% of the elastomeric content are a preferred embodiment of the  
20 invention.

The composition comprising the rubber, the halogenated butyl elastomer and the mineral filler can be cured to obtain a cured product that displays improved properties, for instance in abrasion resistance, rolling resistance and  
25 traction. Curing may be effected with sulfur. The preferred amount of sulfur is 0.3 to 2.0 parts by weight per hundred parts of rubber. There may also be used an activator, for example zinc oxide. If zinc oxide is present it may be present in an amount up to 5 parts, preferably up to 2 parts, by  
30 weight. Other ingredients, for instance stearic acid, or antioxidants, or accelerators may also be added to the

elastomer prior to curing. Sulphur curing is then effected in known manner. See, for instance, chapter 2, "The Compounding and Vulcanization of Rubber", of "Rubber Technology", 3<sup>rd</sup> edition, published by Chapman & Hall, 1995, the disclosure of  
5 which is incorporated by reference.

In yet another aspect, the invention provides a sulphur-cured composition comprising natural rubber and a halogenated elastomer, optionally also containing other elastomers or elastomeric compounds, a filler and a bonding  
10 agent prepared by the processes described above.

By the expression "halogenated butyl elastomer" is meant a chlorinated or brominated butyl elastomer. Brominated elastomers are preferred and the invention is further described, by way of example, with reference to brominated  
15 elastomers. It should be understood, however, that the invention extends to use of a chlorinated butyl elastomer, and references to brominated butyl elastomer should be construed as extending also to chlorinated butyl elastomer unless the context clearly requires otherwise.

20 Brominated butyl elastomers suitable for use in this invention can be obtained by bromination of butyl rubber which is a copolymer of isobutylene and a comonomer that is usually a C<sub>4</sub> to C<sub>6</sub> conjugated diolefin, preferably isoprene. Comonomers other than conjugated diolefins can be used, however, and  
25 mention is made of alkyl-substituted vinyl aromatic comonomers such as C<sub>1</sub>-C<sub>4</sub>-alkyl substituted styrene. One example that is commercially available is brominated isobutylene methylstyrene copolymer (BIMS) in which the comonomer is p-methylstyrene.

A brominated butyl elastomer typically contains from  
30 about 1 to about 3 weight percent of isoprene and from about 97

to about 99 weight percent of isobutylene based on the hydrocarbon content of the polymer, and from about 1 to about 4 weight percent bromine based on the bromobutyl polymer. A typical bromobutyl polymer has a molecular weight, expressed as the Mooney viscosity (ML 1 + 8 at 125°C), of from about 28 to about 55.

For use in the present invention the brominated butyl elastomer preferably contains from about 1 to about 2 weight percent of isoprene and from about 98 to 99 weight percent of isobutylene based on the hydrocarbon content of the polymer and from about 0.5 to about 2.5 weight percent, preferably from about 0.75 to about 2.3 weight percent, of bromine based on the brominated butyl polymer.

A stabilizer may be added to the brominated butyl elastomer. Suitable stabilizers include calcium stearate and epoxidized soyabean oil, preferably used in an amount of from about 0.5 to about 5 parts by weight per 100 parts by weight of the brominated butyl rubber.

Examples of suitable brominated butyl elastomers include Bayer Bromobutyl BB2040, commercially available from Bayer. Bayer Bromobutyl BB2040 has a Mooney viscosity (RPML 1+8 @ 125°C) of  $39 \pm 4$ , a bromine content of  $2.0 \pm 0.3$  wt% and an approximate molecular weight of 500,000 grams per mole. Examples of suitable chlorinated butyl elastomers include Bayer Chlorobutyl CB1240, also commercially available from Bayer. Bayer Chlorobutyl CB1240 has a Mooney viscosity (RPML 1+8 @ 125°C) of  $38 \pm 4$  and a chlorine content of  $1.25 \pm 0.1$  wt%.

The filler used in the blend is composed of particles of a mineral, and examples include silica, silicates, clay such as bentonite, gypsum, alumina, titanium dioxide, talc, mixtures

of these, and the like. These mineral particles have hydroxyl groups on their surface, rendering them hydrophilic and oleophobic. This exacerbates the difficulty of achieving good interaction between the filler particles and the elastomer.

- 5 For many purposes, the preferred mineral is silica, especially silica made by carbon dioxide precipitation of sodium silicate.

Dried amorphous silica particles suitable for use in the elastomeric composition may have a mean agglomerate particle size between 1 and 100 microns, preferably between 10  
10 and 50 microns and most preferably between 10 and 25 microns. It is preferred that less than 10 percent by volume of the agglomerate particles are below 5 microns or over 50 microns in size. A suitable amorphous dried silica moreover has a BET surface area, measured in accordance with DIN (Deutsche  
15 Industrie Norm) 66131, of between 50 and 450 square meters per gram and a DBP absorption, as measured in accordance with DIN 53601, of between 150 and 400 grams per 100 grams of silica, and a drying loss, as measured according to DIN ISO 787/11, of from 0 to 10 percent by weight. Suitable silica fillers are  
20 available under the trademarks HiSil 210, HiSil 233 and HiSil 243 from PPG Industries Inc. Also suitable are Vulkasil S and Vulkasil N, from Bayer AG.

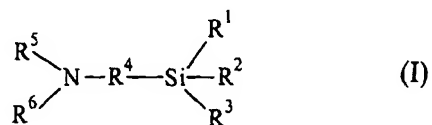
The silane used in the process has a hydroxyl group or a hydrolysable group that is attached to the silicon atom of  
25 the silane. The hydrolysable group can be regarded as a hydroxyl group that is produced in situ from a silane that has a silicon atom that bears a group that will undergo hydrolysis to yield a hydroxyl group on the silicon atom. As examples of such hydrolysable groups there are mentioned particularly  
30 alkoxy groups having up to six carbon atoms, especially ethoxy



and methoxy groups. These and other hydrolysable groups are discussed further below.

The silane is preferably an aminosilane or a sulfur-containing silane. As aminosilanes there are mentioned especially aminosilanes of formula I defined in our PCT international application PCT/CA98/00499, published on 26 November 1998 as WO98/53004, the disclosure of which is incorporated herein by reference, and acid addition salts and quaternary ammonium salts of such aminosilanes.

Formula I of PCT/CA98/00499 is as follows:

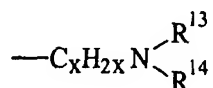


in which:

at least one of  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$ , preferably two of  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  and most preferably three of  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are hydroxyl or hydrolysable groups;

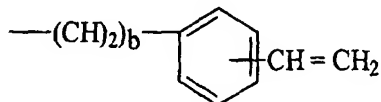
$\text{R}^4$  is a divalent group that is resistant to hydrolysis at the  $\text{Si}-\text{R}^4$  bond;

$\text{R}^5$  is selected from the group consisting of hydrogen; a  $\text{C}_1$ - $\text{C}_{40}$  alkyl group; a  $\text{C}_2$ - $\text{C}_{40}$  mono-, di- or tri-unsaturated alkenyl group; a  $\text{C}_6$ - $\text{C}_{40}$  aryl group; a group of the formula:

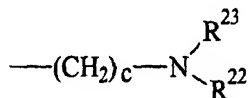


in which x is an integer from 2 to 10,  $R^{13}$  and  $R^{14}$ , which may be the same or different, are each hydrogen;  $C_{1-18}$  alkyl;  $C_{2-18}$  mono-, di- or tri-unsaturated alkenyl; phenyl; a group of the formula:

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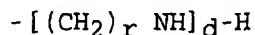


wherein b is an integer from 1 to 10; a group of formula:



10 wherein c is an integer from 1 to 10 and  $R^{22}$  and  $R^{23}$  which may be the same or different, are each hydrogen, a  $C_{1-10}$  alkyl group or  $C_{2-10}$  alkenyl group, provided that there is no double bond in the position alpha to the nitrogen atom; a group of the formula:

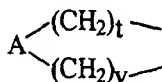
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wherein r is an integer from 1 to 6 and d is an integer from 1 to 4;

$R^6$  may be any of the groups defined for  $R^5$ , or  $R^5$  and  $R^6$  may together form a divalent group of formula:

20



in which A is selected from the group consisting of an oxygen atom and a sulfur atom, -CHR groups and or -NR groups in which R is hydrogen or a  $C_{1-40}$  alkyl or  $C_{2-40}$  alkenyl group, a  $C_6-C_{40}$

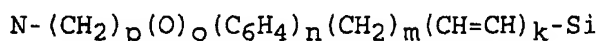
aryl group, and t and v are each independently 1, 2, 3 or 4; provided that the sum of t and v does not exceed 6, and is preferably 4.

In the aminosilane of formula I, it is preferred that  
 5 all three of the groups  $R^1$ ,  $R^2$  and  $R^3$  are readily hydrolysable. Suitable groups  $R^1$  include hydroxyl groups and hydrolysable groups of formula  $OC_pH_{2p+1}$ , where p has a value from 1 to 10. The alkyl chain can be interrupted by oxygen atoms, to give groups, for example, of formula  $CH_3OCH_2O-$ ,  $CH_3OCH_2OCH_2O-$ ,  
 10  $CH_3(OCH_2)_4O-$ ,  $CH_3OCH_2CH_2O-$ ,  $C_2H_5OCH_2O-$ ,  $C_2H_5OCH_2OCH_2O-$ , or  $C_2H_5OCH_2CH_2O-$ . Other suitable hydrolysable groups include phenoxy, acetoxy, chloro, bromo, iodo, ONa, OLi, OK or amino or mono- or dialkylamino, wherein the alkyl group(s) have 1 to 30 carbon atoms.

15  $R^2$  and  $R^3$  can take the same values as  $R^1$ , provided that only one of  $R^1$ ,  $R^2$  and  $R^3$  is chloro, bromo or iodo. Preferably, only one or two of  $R^1$ ,  $R^2$  and  $R^3$  is hydroxyl or ONa, OLi or OK.

Non-limiting examples of groups  $R^2$  and  $R^3$  that are  
 20 not hydrolysable include  $C_{1-10}$  alkyl,  $C_{2-10}$  mono- or diunsaturated alkenyl, and phenyl.  $R^2$  and  $R^3$  can also be a group  $-R^4NR^5R^6$ , discussed further below. It is preferred that  $R^1$ ,  $R^2$  and  $R^3$  are all the same and are  $CH_3O-$ ,  $C_2H_5O-$  or  $C_3H_8O-$ . Most preferably they are all  $CH_3O-$  or  $C_2H_5O-$ .

25 The divalent group  $R^4$  is preferably such that  $N-R^4-Si$  is one of the formula:



in which k, m, n, o and p are all whole numbers. The order of the moieties between N and Si is not particularly restricted, other than that neither N or O should be directly bound to Si. The value of k is 0 or 1, the value of m is from 0 to 20 inclusive, the value of n is 0, 1 or 2, the value of o is 0 or 1 and the value of p is from 0 to 20 inclusive, with the provisos that the sum of the values of k, m, n, o and p is at least 1 and not more than 20 and that if o is 1, p is 1 or greater and the sum of k, m and n is 1 or greater, i.e. that the Si atom is linked directly to a carbon atom. There should be no hydrolysable bond between the silicon and nitrogen atoms. Preferably, m is 3 and 1, n, o and p are all 0, i.e., R<sup>4</sup> is -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-.

The group R<sup>5</sup> is preferably a C<sub>8-20</sub> mono-unsaturated alkenyl group, most preferably a C<sub>16-18</sub> monounsaturated alkenyl group. R<sup>6</sup> is preferably hydrogen.

Suitable aminosilanes of Formula I include, but are not limited to:

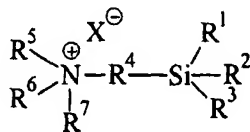
- 3-aminopropylmethyldiethoxysilane,
- N-2-(vinylbenzylamino)-ethyl-3-aminopropyl-trimethoxysilane,
- N-(2-aminoethyl)-3-aminopropyltrimethoxysilane,
- trimethoxysilylpropyldiethylenetriamine,
- N-2-(aminoethyl)-3 aminopropyltris(2-ethylhexoxy)-silane,
- 3-aminopropyldiisopropylethoxysilane,
- N-(6-aminohexyl)aminopropyltrimethoxysilane,

- 4-aminobutyltriethoxysilane,
- 4-aminobutyldimethylmethoxysilane, triethoxy-  
silylpropyl-diethylenetriamine,
- 3-aminopropyltris(methoxyethoxyethoxy)silane,
- 5 N-(2-aminoethyl)-3-aminopropyltrimethoxysilane,
- N-2-(aminoethyl)-3-aminopropyltris(2-ethylhexoxy)-  
silane,
- 3-aminopropyldiisopropylethoxysilane,
- N-(6-aminoethyl)aminopropyltrimethoxysilane,
- 10 4-aminobutyltriethoxysilane, and
- (cyclohexylaminomethyl)-methyldiethoxysilane.

Preferred compounds of formula I include those in which  $R^5$  is hydrogen and  $R^6$  is the alkenyl group from the following: soya alkyl, tall oil alkyl, stearyl, tallow alkyl,  
15 dihydrogenated tallow alkyl, cocoalkyl, rosin alkyl, and palmityl, it being understood that in this case the alkyl may include unsaturation.

It is preferred that at least one of  $R^4$ ,  $R^{13}$  and  $R^{14}$  has a chain of at least 8 carbon atoms, more preferably at  
20 least 10 carbon atoms, uninterrupted by any heteroatom.

The aminosilane of formula I can be used as the free base, or in the form of its acid addition or quaternary ammonium salt, i.e.



wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> are as defined above; R<sup>7</sup> is selected from the group consisting of hydrogen, C<sub>1-40</sub> alkyl groups and C<sub>2-40</sub> mono-, di- or triunsaturated alkenyl groups, and X is an anion. X is suitably chlorine, bromine, or sulphate, of which chlorine and bromine are preferred, and R<sup>7</sup> is preferably hydrogen.

Non-limiting examples of suitable salts of aminosilanes of formula I include

- N-oleyl-N-[(3-triethoxysilyl)propyl]ammonium chloride,
- N-3-aminopropylmethyldiethoxy-silane hydrobromide,
- (aminoethylaminomethyl)phenyltrimethoxysilane hydrochloride,
- N-[(3-trimethoxysilyl)propyl]-N-methyl,
- N-N-diallylammonium chloride,
- N-tetradecyl-N,N-dimethyl-N-[(3-trimethoxysilyl)propyl]ammonium bromide,
- 3[2-N-benzylaminoethyl-aminopropyl]trimethoxysilane hydrochloride,
- N-octadecyl-N,N-dimethyl-N-[(3-tri-methoxysilyl)propyl]ammonium bromide,
- N-[(trimethoxysilyl)propyl]-N-tri(n-butyl)ammonium chloride,
- N-octadecyl-N-[3-triethoxysilyl]propyl]ammonium chloride,

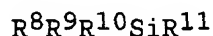
N-2-(vinylbenzylamino)ethyl-3-aminopropyl-trimethoxysilane hydrochloride,

N-2-(vinylbenzylamino)ethyl-3-aminopropyl-trimethoxysilane hydrochloride and

- 5 N-oleyl-N-[(3-trimethoxysilyl)propyl]ammonium chloride.

The silane compound may be a sulfur-containing silane compound. Suitable sulfur-containing silanes include those described in United States patent 4,704,414, in published  
 10 European patent application 0,670,347 A1 and in published German patent application 4435311 A1, the disclosures of each of which is incorporated herein by reference. One suitable compound is a mixture of bis[3-(triethoxysilyl)propyl]-monosulfane, bis[3-(triethoxysilyl)propyl] disulfane, bis[3-  
 15 (triethoxysilyl)propyl]trisulfane and bis[3-(triethoxysilyl)propyl]tetrasulfane and higher sulfane homologues available under the trademarks Si-69 (average sulfane 3.5), Silquest™ A-1589 (from CK Witco) or Si-75 (from Degussa) (average sulfane 2.0). Another example is bis[2-  
 20 (triethoxysilyl)ethyl]-tetrasulfane, available under the trademark Silquest RC-2.

Examples of suitable sulfur-containing silanes include compounds of formula



- 25 in which at least one of  $R^8$ ,  $R^9$  and  $R^{10}$ , preferably two of  $R^8$ ,  $R^9$  and  $R^{10}$  and most preferably three of  $R^8$ ,  $R^9$  and  $R^{10}$ , are hydroxyl or hydrolysable groups. The groups  $R^8$ ,  $R^9$  and  $R^{10}$  are bound to the silicon atom. The group  $R^8$  may be hydroxyl or

OC<sub>p</sub>H<sub>2p+1</sub> where p is from 1 to 10 and the carbon chain may be interrupted by oxygen atoms, to give groups, for example of formula CH<sub>3</sub>OCH<sub>2</sub>O-, CH<sub>3</sub>OCH<sub>2</sub>OCH<sub>2</sub>O-, CH<sub>3</sub>(OCH<sub>2</sub>)<sub>4</sub>O-, CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>O-, C<sub>2</sub>H<sub>5</sub>OCH<sub>2</sub>O-, C<sub>2</sub>H<sub>5</sub>OCH<sub>2</sub>OCH<sub>2</sub>O-, or C<sub>2</sub>H<sub>5</sub>OCH<sub>2</sub>CH<sub>2</sub>O-. Alternatively,

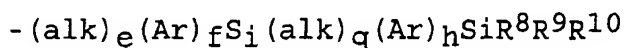
5 R<sup>8</sup> may be phenoxy. The group R<sup>9</sup> may be the same as R<sup>8</sup>. R<sup>9</sup> may also be a C<sub>1-10</sub> alkyl group, or a C<sub>2-10</sub> mono- or diunsaturated alkenyl group. Further, R<sup>9</sup> may be the same as the group R<sup>11</sup> described below.

R<sup>10</sup> may be the same as R<sup>8</sup>, but it is preferred that

10 R<sup>8</sup>, R<sup>9</sup> and R<sup>10</sup> are not all hydroxyl. R<sup>10</sup> may also be C<sub>1-10</sub> alkyl, phenyl, C<sub>2-10</sub> mono- or diunsaturated alkenyl. Further, R<sup>10</sup> may be the same as the group R<sup>11</sup> described below.

The group R<sup>11</sup> attached to the silicon atom is such that it may participate in a crosslinking reaction with

15 unsaturated polymers by contributing to the formation of crosslinks or by otherwise participating in crosslinking. R<sup>11</sup> may have the following structure:



where R<sup>8</sup>, R<sup>9</sup> and R<sup>10</sup> are the same as previously defined, alk is

20 a divalent straight hydrocarbon group having between 1 and 6 carbon atoms or a branched hydrocarbon group having between 2 and 6 carbon atoms, Ar is either a phenylene -C<sub>6</sub>H<sub>4</sub>-, biphenylene -C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>- or -C<sub>6</sub>H<sub>4</sub>-OC<sub>6</sub>H<sub>4</sub>-group and e, f, g and h are either 0, 1 or 2 and i is an integer from 2 to 8 inclusive

25 with the provisos that the sum of e and f is always 1 or greater than 1 and that the sum of g and h is also always 1 or greater than 1. Alternately, R<sup>11</sup> may be represented by the



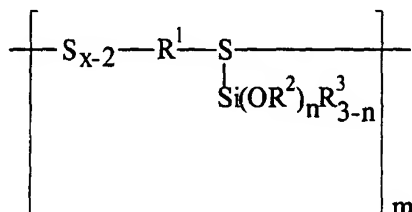
structures  $(\text{alk})_e(\text{Ar})_f\text{SH}$  or  $(\text{alk})_e(\text{Ar})_f\text{SCN}$  where  $e$  and  $f$  are as defined previously.

Preferably,  $\text{R}^8$ ,  $\text{R}^9$  and  $\text{R}^{10}$  are all either  $\text{OCH}_3$ ,  $\text{OC}_2\text{H}_5$  or  $\text{OC}_3\text{H}_7$  groups and most preferably all are  $\text{OCH}_3$  or  $\text{OC}_2\text{H}_5$  groups. It is most preferred that the sulfur-containing silane is bis[3-(trimethoxysilyl)propyl]-tetrasulfane (Si-168).

Non-limiting illustrative examples of other sulfur-containing silanes include the following:

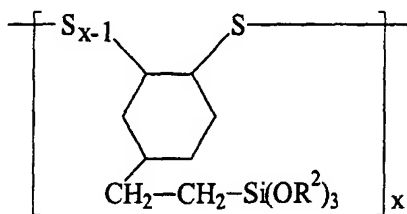
bis[3-(triethoxysilyl)propyl]disulfane,  
 10 bis[2-(trimethoxysilyl)ethyl]tetrasulfane,  
 bis[2-(triethoxysilyl)ethyl]trisulfane,  
 bis[3-(trimethoxysilyl)propyl]disulfane,  
 3-mercaptopropyltrimethoxysilane,  
 3-mercaptopropylmethyldiethoxysilane, and  
 15 3-mercaptoethylpropylethoxymethoxysilane.

Other preferred sulfur-containing silanes include those disclosed in published German patent application 44 35 311 A1, the disclosure of which is incorporated by reference. On pages 2 and 3, there is disclosure of oligomers and polymers of sulphur containing organooxysilanes of the general formula:



- in which  $R^1$  is a saturated or unsaturated, branched or unbranched, substituted or unsubstituted hydrocarbon group that is at least trivalent and has from 2 to 20 carbon atoms, provided that there are at least two carbon-sulphur bonds,  $R^2$  and  $R^3$ , independently of each other, are saturated or unsaturated, branched or unbranched, substituted or unsubstituted hydrocarbon groups with 1 to 20 carbon atoms, halogen, hydroxy or hydrogen,  $n$  is 1 to 3,  $m$  is 1 to 1000,  $p$  is 1 to 5,  $q$  is 1 to 3 and  $x$  is 1 to 8.

- 10 Other sulfur-containing silanes are of the general formula

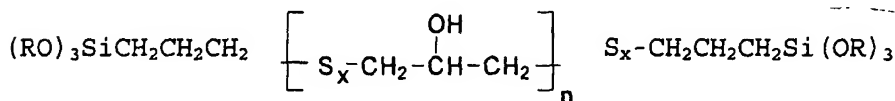


- 15 wherein  $R^2$ ,  $m$  and  $x$  have the meanings given above, and  $R^2$  is preferably methyl or ethyl. These compounds disclosed are in German Patent Application No. 44 35 311 A1.

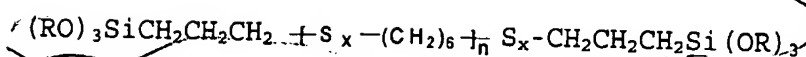
Particularly preferred sulfur-containing silanes are those of the following general formulae:

- 20  $(\text{RO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2 \text{---} \text{S}_x\text{---CH}_2\text{CH}_2 \text{---} \text{S}_x\text{---CH}_2\text{CH}_2\text{CH}_2\text{Si(OR)}_3$

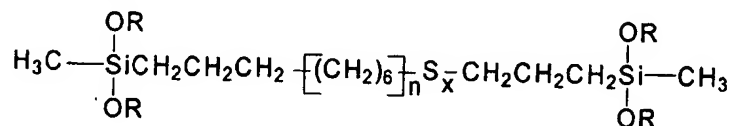
in which  $R = -\text{CH}_3$  or  $-\text{C}_2\text{H}_5$ ,  $x=1-6$  and  $n=1-10$ ;



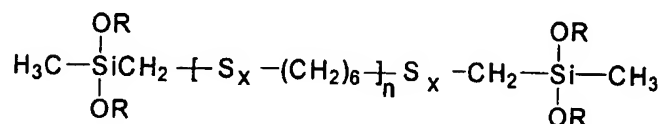
in which  $R = -\text{CH}_3$  or  $-\text{C}_2\text{H}_5$ ,  $x = 1-6$  and  $n = 1-10$ ;



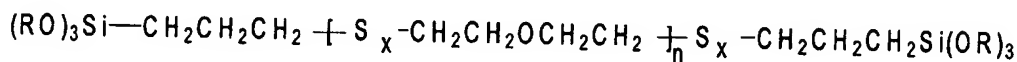
in which R = -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub> or -C<sub>3</sub>H<sub>7</sub>, n = 1-10 and x = 1-6;



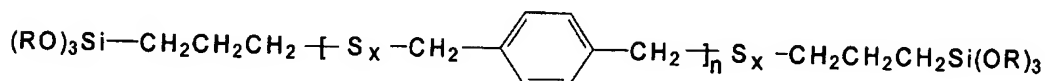
5 in which R = -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub> or -C<sub>3</sub>H<sub>7</sub>, n = 1-10 and x = 1-6;



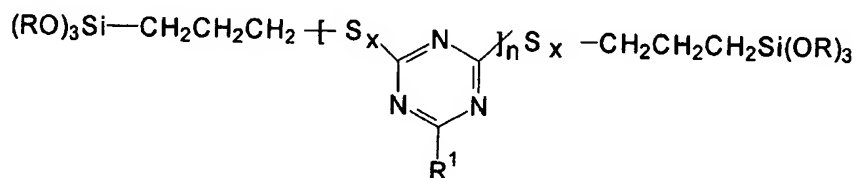
in which R = -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub>, -C<sub>3</sub>H<sub>7</sub>, n = 1-10 and x = 1-6;



10 in which R = -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub>, -C<sub>3</sub>H<sub>7</sub>, n = 1-10 and x = 1-6;

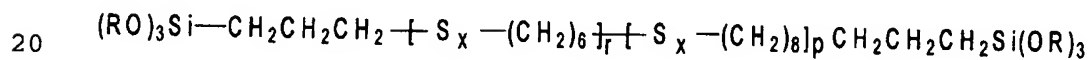


in which R = -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub> or -C<sub>3</sub>H<sub>7</sub>, n = 1-10 and x = 1-6;



15

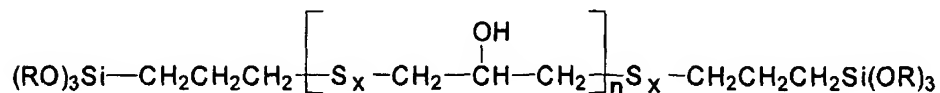
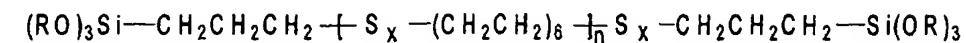
in which R = -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub> or -C<sub>3</sub>H<sub>7</sub>; R<sup>1</sup> = -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub>, -C<sub>3</sub>H<sub>7</sub>, -C<sub>5</sub>H<sub>5</sub>, -OCH<sub>3</sub>, -OC<sub>2</sub>H<sub>5</sub>, -OC<sub>3</sub>H<sub>7</sub> or -OC<sub>5</sub>H<sub>5</sub>, n = 1-10 and x = 1-8; and



20

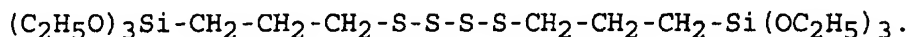
in which R = -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub> or -C<sub>3</sub>H<sub>7</sub>, r+p = 2-10 and x = 1-6.

Also mentioned are sulfur-containing silanes of the formulae:



5 in which x is 1-6 and n is 1-4.

If the silane is a sulfur-containing silane a preferred silane is bis[3-(triethoxysilyl)propyl]-tetrasulfane, of formula

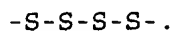


- 10 This compound is commercially available under the trade-mark Si-69. In fact Si-69 is a mixture of the above compound, i.e., the tetrasulfane, with bis[3-(triethoxy-silyl)-propyl]monosulfane and bis[3-(triethoxysilyl)-propyl]trisulfane, average sulfane 3.5.

Another preferred sulfur-containing silane is available under the trade-mark Silquest 1589. The material available under this trade-mark is a mixture of sulfanes but the predominant component, about 75%, is similar in structure to the tetrasulfane Si-69, except that it is a disulfane, i.e., it has only



- 15 where Si-69 has



The remainder of the mixture is composed of  $-S_1$  to  $-S_7-$  compounds. Silquest A-1589 is available from CK Witco. A

similar material is available from Degussa under the trade-mark Si-75.

Yet another preferred sulfur-containing silane is bis[2-(triethoxysilyl)ethyl]tetrasulfane, available under the  
5 trade-mark Silquest RC-2.

The trimethoxy compounds corresponding to these triethoxy compounds can also be used.

The amount of filler to be incorporated into the elastomeric composition can be varied between wide limits.  
10 Typical amounts of filler are about 20 parts to about 120 parts by weight, preferably 30 parts to 100 parts, more preferably 40 to 80 parts per hundred parts of elastomer. The amount of the silane compound or compounds used may be about 2 to 12 parts, preferably 6 to 10 parts, per hundred parts of filler. There  
15 may also be present up to about 40 parts of processing oil, preferably 5 to 20 parts, per hundred parts of elastomer, and a lubricant, for example a fatty acid such as stearic acid up to about 3 parts by weight, preferably up to 2 parts by weight.

Carbon black is not normally used as a filler in the  
20 elastomer compositions of the invention, but in some embodiments it may be present in an amount up to about 40 phr. If the mineral filler is silica and it is used with carbon black, the silica should constitute at least 55% by weight of the total of silica and carbon black. If the halobutyl  
25 elastomer/natural rubber composition of the invention is blended with a further elastomeric composition, that further elastomeric composition may contain carbon black as a filler, or may contain mineral filler, or it may be unfilled until it is blended with the other components of the composition.

The butyl elastomer, natural rubber filler and silane are mixed together, suitably at an elevated temperature that may range from about 30°C to about 200°C. It is preferred that the temperature is greater than about 60°C, and a temperature in the range 90 to 160°C is particularly preferred. Normally the mixing time does not exceed about one hour and a time in the range from about 2 to 30 minutes is usually adequate. The mixing is suitably carried out in an internal mixer such as a Banbury mixer, or a Haake or Brabender miniature internal mixer. A two roll mill mixer also provides a good dispersion of the filler within the elastomeric composition. An extruder also provides good mixing, and permits shorter mixing times. It is possible to carry out the mixing in two or more stages, and the mixing can be done in different apparatus, for example one stage in an internal mixer and one stage in an extruder. Total mixing time to achieve blends may vary depending on the particular silane selected or bonding agent, the relative amounts of elastomers in a given blend, and the degree of incorporation of silica desired.

It is possible to pre-treat the mineral filler with the bonding agent. Thus, for example, halobutyl elastomer, natural rubber, mineral filler and bonding agent may be added separately and then all be blended together. Alternatively the silica may be treated with the bonding agent prior to being blended with the halobutyl elastomer and natural rubber.

In a preferred embodiment of the invention halobutyl elastomer, silica particles, silane and, optionally, processing oil extender are placed in a mixer such as a Banbury mixer, and mixed. It is preferred that the temperature of the mixing is  
5 not too high and preferably does not exceed about 160°C. Higher temperatures may cause curing to proceed undesirably far and

impede subsequent processing. The product of mixing these four ingredients at a temperature not exceeding about 160°C can be readily further processed on a warm mill with the addition of the natural rubber and the addition of further curatives such as sulfur as vulcanizing agent, zinc oxide as activator and magnesium oxide to raise basicity. Alternatively, the two elastomers, i.e., the natural rubber and the halogenated butyl elastomer may be admixed in one masterbatch with the other ingredients in the Banbury mixer before further processing.

10 Curing can be effected with sulfur as vulcanizing agent. Other curing agents can be used, however. As examples of other curing agents there are mentioned bis-dienophiles such as bis-maleimide, commercially available from DuPont under the trademark HVA 2. Other commercially available ingredients that  
15 can be present in the masterbatch include processing aids such as aromatic oils (Sundex 790) and waxes (Sunolite 240), antioxidants (Vulkanox 4020 LG 6PPD and Vulkanox H5 Pastille (TMQ)), scorch inhibitors (Santogard PVI WGR-80%) and accelerators (Vulkacit C2/Eg-C(CBS)).

The elastomer compositions of the invention find many uses, but mention is made particularly of use in tire tread compositions for vehicles, especially trucks and buses engine movements, shoes, rubber diaphragms such as for water pumps.

20 Important features of a tire tread composition are that it shall have low rolling resistance, good traction, particularly in the wet, and good abrasion resistance so that it is resistant to wear. Compositions of the invention display these desirable properties. Thus, an indicator of traction is  
25  $\tan \delta$  at 0°C, with a high  $\tan \delta$  at 0°C correlating with good traction. An indicator of rolling resistance is  $\tan \delta$  at 60°C, with a low  $\tan \delta$  at 60°C correlating with low rolling

resistance. Rolling resistance is a measure of the resistance to forward movement of the tire, and low rolling resistance is desired to reduce fuel consumption. Low values of loss modulus  $E''$  at 60°C are also indicators of low rolling resistance. As is demonstrated in the examples below, compositions of the invention display high  $\tan \delta$  at 0°C, low  $\tan \delta$  at 60°C and low loss modulus at 60°C.

The elastomeric compositions of this invention can be further mixed with other rubbers, for example, butadiene rubber, styrene-butadiene rubber and isoprene rubbers, and compounds contain these elastomers.

The invention is further illustrated in the following examples and the accompanying Figures 1 and 2.

Description of tests:

15 Abrasion resistance: DIN 53-516 (60 grit Emery paper)

DYNAMIC PROPERTY TESTING

Dynamic testing ( $\tan \delta$  at 0°C and 60°C, Loss modulus at 60°C) were carried out using the Rheometrics RSA II. The RSA II is a dynamic mechanical analyzer for characterizing the properties of vulcanized elastomeric materials.

The dynamic mechanical properties give a measure of traction with the best traction usually obtained with high values of  $\tan \delta$  at 0°C. Low values of  $\tan \delta$  at 60°C., and in particular, low loss modulus at 60°C. are indicators of low rolling resistance.

Cure rheometry: ASTM D 52-89 MDR2000E Rheometer at 3° arc and 1.7 Hz



Permeability: ASTM D 14-34

The invention is further illustrated in the following examples and accompanying drawings.

Description of Ingredients and General Mixing Procedure:

5 HiSil 233 - silica - a product of PPG

The halobutyl elastomer, natural rubber, silica and silane compounds were mixed in a model B Banbury mixer with a nominal volume of 1570 milliliters and using a fill factor of nominally 67% to 73% by volume. The starting temperature was  
10 40°C.

At 0 minutes, the rubber was added to the Banbury followed by the oil + 1/2 of the silica + 1/2 of the silane. The ram was lowered and the Banbury turned on at 77rpm.

At 1 minute, a 1/4 of the silica was added.

15 At 2 minutes, the remainder of the silane and the remainder of the silica were added.

After 4 minutes the Banbury chute was swept.

The products were mixed for a total of 6 minutes at  
120 - 145°C.

20 The compound was removed from the Banbury, and sheeted out on a warm mill set at 40°C.

Curatives were then added to all or a portion of the compound on a mill set at 30°C.

Example 1:

Single masterbatches containing both brominated butyl rubber (BB 2040), natural rubber, silica, 3-aminopropyl-triethoxysilane and bis[3-(triethoxysilyl)propyl]tetrasulfane (Si 69) were prepared. The elastomers were used in the ratios 100/0, 90/10, 80/20, 70/30, 50/50, 25/75 and 0/100. The ratio of the two silanes was also varied, and one 50/50 blend of elastomers was prepared with no silane.

The components were mixed in a white "B" Banbury, utilizing a 6 minute mix. Dump temperatures varied between 120°C and 140°C for the components containing silanes. The compound containing no silane reached a dump temperature of 150°C.

The mixing conditions were;

0' add BIIR +  $\frac{1}{2}$  HiSil 233 +  $\frac{1}{2}$  bonding agent

1' add  $\frac{1}{4}$  HiSil 233

2' add  $\frac{1}{4}$  HiSil 233 +  $\frac{1}{2}$  bonding agent

3-4' sweep

6' dump

The curatives, which were added on a cool mill, were

Santogard PVI WGR-80%	0.5
NBS Sulfur	1.8-1
Vulkazit CZ/EG-C (CBS)	1.8-1
ZnO	4-1

The complete formulations are given in Table 2.

TABLE 1

POLYSAR BROMOBUTYL BB2040 (J-11575)

SMR CV60 NATURAL RUBBER

HI-SIL 233

MB 99CW60

SILANE SI-69

STEARIC ACID EMERSOL 132 NF

SUNDEX 790

SUNOLITE 240

VULKANOX 4020 LG (GPPD)

VULKANOX HS PASTILLE (GRANULAR) (TMQ)

HI-SIL 233

	10	20	30	50	75	100	50
100	90	80	70	50	25	0	50
30	30	30	30	30	30	30	30
0	0.4	0.8	1.2	2	3	4	0
3	2.7	2.4	2.1	1.5	0.75	0	0
2	2	2	2	2	2	2	2
4	4	4	4	4	4	4	4
1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
2	2	2	2	2	2	2	2
2	2	2	2	2	2	2	2
15	15	15	15	15	15	15	15

TABLE 1 CONTINUED

HI-SIL 233	15	15	15	15	15	15	15	15	15
MB 99CWXX60	0	0.4	0.8	1.2	2	3	4	0	
SILANE SI-69	3	2.7	2.4	2.1	1.5	0.8	0	0	
Total SI69	6	5.4	4.6	4.2	3.0	1.5	0.0	0.0	
Total amino propyl triethoxy silane (MB 99CWXX60)	0	0.8	1.6	2.4	4.0	6.0	8.0	0.0	
Total HiSil 233	60	60	60	60	60	60	60	60	
SANTOGARD PVI (PELLETIZED) WGR-80%	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	
SULFUR NBS	1.80	1.72	1.64	1.56	1.40	1.20	1.00	1.40	
VULKACIT CZ/EG-C (CBS)	1.80	1.72	1.64	1.56	1.40	1.20	1.00	1.40	
ZINC OXIDE (KADOX 920) GRADE PC 216 (C&PT STD)	4.00	3.70	3.40	3.10	2.50	1.75	1.00	2.50	

The effect of addition of BB2040 to natural rubber on abrasion and  $\tan \delta$  at 0°C is shown in Figure 1. As can be seen, addition of the halobutyl elastomer to natural rubber in amounts up to 30% has no effect on abrasion resistance, but  
5  $\tan \delta$  at 0°C is increased from 0.11 to 0.19, indicating a significant improvement in wet traction without any adverse effect on abrasion resistance.

The effect of addition of BB2040 to natural rubber on the dynamic properties is shown in Figure 2. This shows  $\tan \delta$   
10 at 0°C increasing with the halobutyl elastomer content, again indicating an increase in wet traction.  $\tan \delta$  at 60°C remains constant but the loss modulus  $E''$  ranges between 1.47 and 1.96 with amounts of halobutyl elastomer from 10 to 30%. These values compare favorably with a value of  $E''$  of 2.36 for 100%  
15 natural rubber.

CLAIMS:

1. An elastomeric composition comprising natural rubber, a halobutyl elastomer, a mineral filler, and a rubber-mineral filler bonding agent.
- 5 2. A composition according to claim 1 wherein the halobutyl elastomer is a bromobutyl elastomer and the filler is silica.
3. A composition according to claim 1 or 2 wherein the bonding agent is a silane.
- 10 4. A composition according to claim 1, 2 or 3 wherein the composition is cured with sulphur.
5. A composition according to any one of claims 1 to 4 wherein the halobutyl elastomer constitutes from 5 to 50% of the elastomeric content of the composition.
- 15 6. A composition according to claim 5 wherein the halobutyl elastomer constitutes from 5 to 30% of the elastomeric content of the composition.
7. A process for preparing an elastomeric composition which comprises blending a natural rubber, a halobutyl  
20 elastomer, a mineral filler and a rubber-mineral filler bonding agent.
8. A process according to claim 8 wherein natural rubber, halobutyl elastomer, mineral filler and bonding agent are added separately to the blend.
- 25 9. A process according to claims 7 or 8 wherein the mineral filler is silica and the bonding agent is a silane that has at least one hydroxyl group or hydrolysable group attached to a silicon atom of the silane.

10. A process according to claim 9 wherein the silane is aminopropyltriethoxysilane, bis[3-(triethoxysilyl)propyl]-tetrasulfane, bis[3-(triethoxysilyl)propyl]disulfane or mercaptopropyl trimethoxysilane, or a mixture of two or more of these.

11. A cured, filled elastomeric composition according to any one of claims 1 to 6 in the form of a tire tread for a vehicle.

12. A cured, filled elastomeric composition according to any one of claims 1 to 6 in the form of a tire tread for a truck.

13. A cured, filled elastomeric composition according to any one of claims 1 to 6 in the form of an engine mount, a shoe sole or a diaphragm for a pump.

SMART & BIGGAR

OTTAWA, CANADA

PATENT AGENTS

EFFECT OF BB2040 CONTENT ON ABRASION AND TAN DELTA AT 0°C.

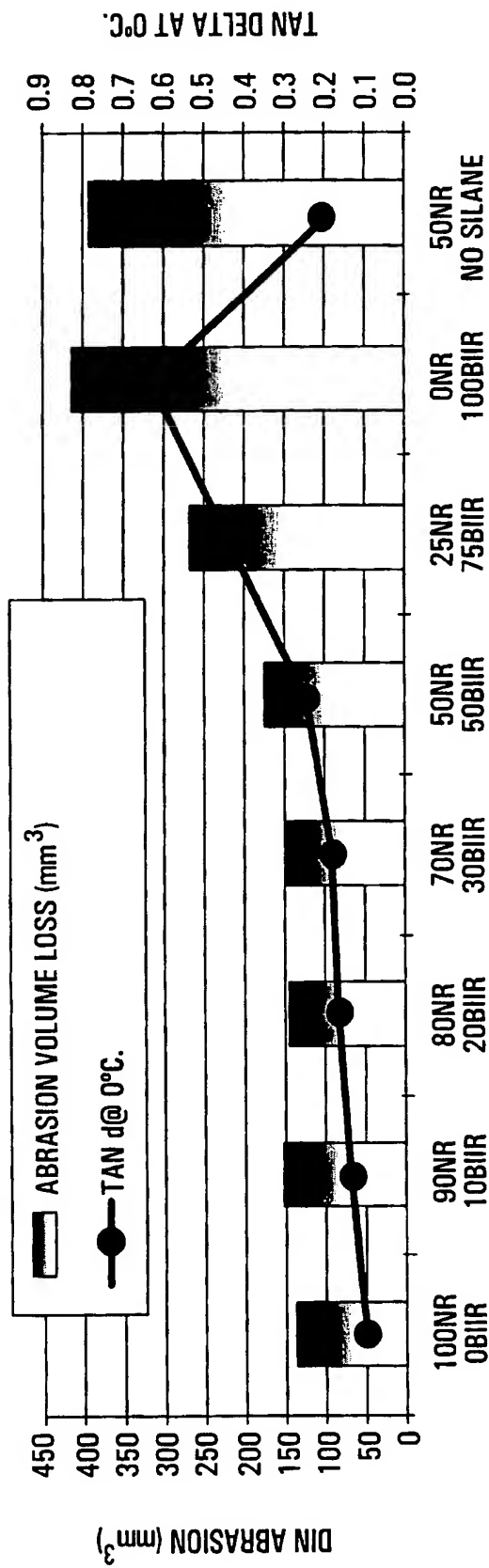


FIG. 1



EFFECT OF ADDITION OF BIIR TO NR ON THE DYNAMIC PROPERTIES

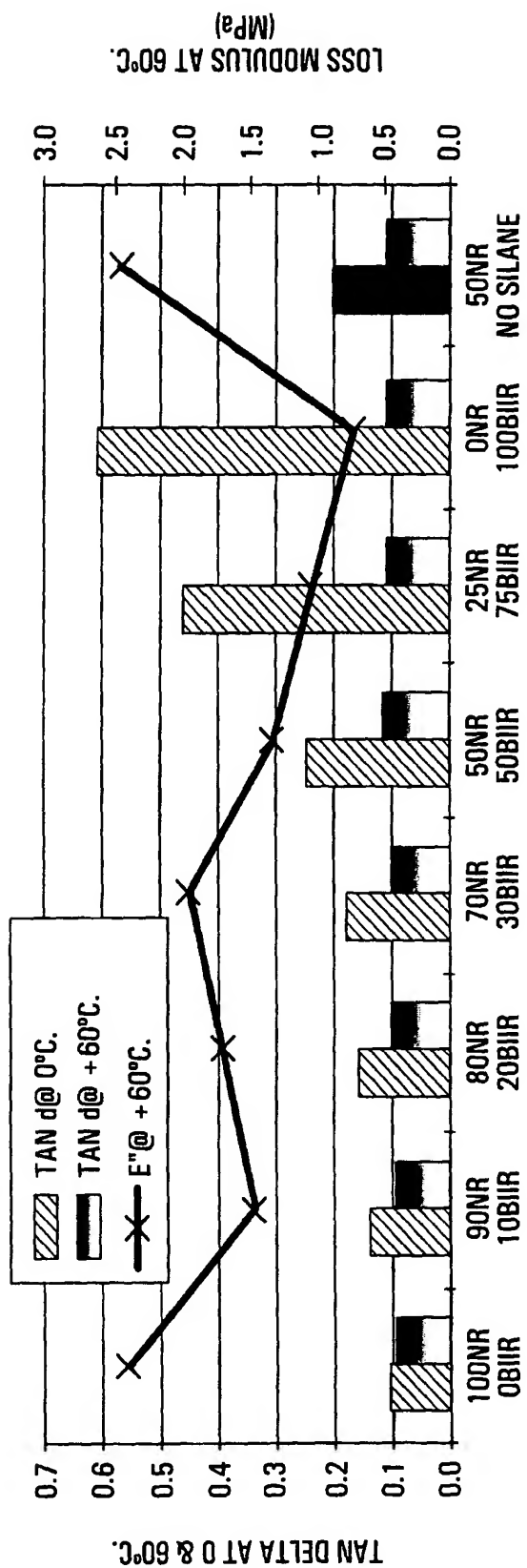


FIG. 2

